REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION IN THE DISTRIBUTION SYSTEM

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ABSTRACT

Currently, the first casualties after an intentional contamination event will be identified by physicians or other health care providers due to the onset of symptoms well after exposure. One approach to mitigating this potential disaster includes on-line monitoring of drinking water distribution systems. Four credible threat drinking water contaminants (aldicarb, sodium arsenate, sodium cyanide, and sodium fluoroacetate) were added to tap water and analyzed at different concentrations to determine their detectability in a drinking water distribution system. Bench top analysis and on-line monitoring equipment was used to measure pH, chlorine residual, turbidity, and total organic carbon values before and after introduction of these contaminants. Results indicate that all four contaminants can be detected at relatively low concentrations. Three of the four contaminants were detected below a concentration that will cause significant health impact.

INTRODUCTION

United States drinking water systems are among the greatest engineering and public health accomplishments of the 20th century (Luthy, 2002). It is often taken for granted that when the faucet is turned on, safe water will flow. Concerns over the safety of drinking water, and the security of drinking water distribution systems date back to approximately 300 B.C. during the construction of *Aqua Appia*, one of the aqueducts of the Roman Empire. The Romans were concerned that their water supply systems would be rendered useless by enemy action. To avert this threat, some of their aqueducts were buried up to 50 feet in the ground (Herschel, 1973).

President Clinton signed Executive Order 13010 in 1996 designating water supply systems as one of eight critical infrastructures, "so vital that their incapacity or destruction would have a debilitating impact on the defense or economic security of the United States" (Federal Register, 1996). President Bush signed the Public Health Security and Bioterrorism Preparedness and Response Act into law in 2002 recognizing that, among other things, drinking water systems are vulnerable to intentional acts of sabotage, and that community water systems serving more than 3,300 customers need to take appropriate action to protect public health.

Eighty percent of the US population is served by 14% of the utilities (Clark et al., 2002). This highlights the impact that an act of sabotage to a large drinking water system may have. Water distribution networks have been identified as a major vulnerability. The distribution system is uniquely vulnerable because of its accessibility to those it serves, and the geographic area that it reaches. Khan et al. (2001) highlight the fact that except in the case of aerosols, food or water contamination is the easiest way to distribute chemical and biological agents. Due to the population that a drinking water distribution system serves, a large number of casualties would occur over a wide geographic area. This is particularly alarming when three weeks pass before a source of contamination is identified, as was displayed during the cryptosporidiosis outbreak in Milwaukee during 1993. This incident in and of itself demonstrated the potential for drinking water to serve as a conveyance for spread of the disease.

These incidents affirm the value to public health that an early warning system in the distribution system might have. Early detection of a chemical or biological contamination event is crucial, and could save lives. The use of new agents, combinations of agents, or contaminants that haven't been seriously considered in the past is a very plausible terrorist approach and

therefore, the use of surrogates for detection, to cast a broader net, is one approach that needs to be investigated. Early detection is absolutely essential.

This view was highlighted by the National Research Council (2002), who recognized that forced entry of a highly toxic contaminant into the distribution system could have serious consequences. They further declared that monitoring and identification of biological and chemical agents is among the four highest-priority areas for research on water security. Similarly, Luthy (2002) emphasized the importance of protecting water quality by expediting the detection of contaminants to minimize impacts to human health. The use of multiple barriers in the distribution system, versus just a residual oxidant, was identified as a valid requirement. On-line detection using water quality surrogates for contaminant detection may be considered an additional barrier in the distribution system.

The development and use of real-time monitoring was also recommended by Parmlee (2002) and States et. al (2003) to protect against bioterrorism in water systems. This recommendation was validated when the USEPA awarded a $500,000 project to the USGS to set up real-time monitoring equipment at two drinking water systems in New Jersey (USEPA, 2002). The significance of this effort is best captured in the USEPA's quote at the onset of the project, "Whether a contaminant enters a water supply system by terrorist action or by accident, it is vital that we have the information to respond quickly. That's why real-time monitoring offers such great promise." In addition, it was emphasized that real-time monitoring will allow water system operators to be aware of potentially dangerous situations before contaminated water reaches consumer taps. Finally, Deininger et al. (2000) summarize it best, "strategically placed monitors in a distribution system is the obvious solution for the protection of a water supply system."

The threat of chemical or microbiological contamination to drinking water is well established, and would be an effective way of causing devastating public health consequences. As it presently stands, the technology to detect these contaminants is lacking. Early detection of these contaminants via on-line or real-time monitoring has been identified as a feasible way to provide early warning to protect public health. This research is a first step to address the challenge of detecting a large number of potential contaminants in a drinking water distribution system real-time. The basic premise of this research is that readily available and relatively inexpensive equipment can be used to determine real-time when a contamination event in a distribution system has occurred, with the intent being to provide an early warning so that public health is protected.

METHODS & MATERIALS

Experiments were conducted using actual distribution system water with both batch and continuous-flow data collection events. After determining the baseline water quality with real-time, on-line instruments, model contaminants were added to batch and pilot scale distributions systems to determine the level of detection with different water quality parameters.

Baseline water quality data. Running tap water, via a one-inch PVC pipe loop, was connected to two on-line water quality panels (Figure 1): a multi-instrument panel that measured pH, turbidity, conductivity, and chlorine residual[1]; and one that measured TOC[2]. Data were collected once per minute using datalogger software[3], collecting over 16,000 data points. This data was used to determine what represents "normal" water quality in the distribution system, and to estimate the population standard deviation. In addition, some general information about the distribution of the data was provided, as well as summary statistics.

Distribution system water quality fluctuates with temperature, seasonal source water quality, flow, demand, and water treatment plant operations. Taking this into consideration, additional 100-minute baselines were collected just prior to the introduction of contaminants into the bench scale distribution system. This allowed for the comparison of the contaminated water with a baseline established immediately before the contaminants were added.

The on-line instruments required up to two hours to warm up before readings were considered valid. For this study, the water quality panel and the TOC panel were both started at least 12 hours before any data was obtained. In addition, on-line instruments that measure pH[4] and chlorine residual[5] were calibrated against bench top analytical equipment on a daily basis. The TOC panel, turbidimeters[6,7], and conductivity probe[8] were all calibrated before they were placed in service.

Miller and Miller (2000) define the limit of detection as being equal to the blank signal, y_B, plus three standard deviations of the blank, or

$$\text{Limit of detection} = y_B + 3s_B \qquad (1)$$

In this case, the "blank" signal is zero, as the *difference* between baseline conditions and the addition of a contaminant is what's being measured, leaving three standard deviations as the limit of detection.

The baseline is key to determining the normal signal variation. Normally distributed data will result in 99.96% of the points falling within three standard deviations from the mean (x-bar ± 3-sigma) when only considering random variability. Anything outside of three standard deviations (3-sigma) represents an anomaly, and should be addressed accordingly (there is a 4 in

10,000 chance that the anomaly is a false positive). The standard deviation in the baseline data will be used to compare beaker test data to the 3-sigma values to determine a limit of detection. This will provide the first indication of the potential of using water quality parameters as surrogates to detect a contamination event. Similarly, baseline data will also be collected for 100 minutes immediately before the introduction of contaminants into the distribution system. This will ensure that the baseline data is representative of system conditions when the experiments were conducted.

Contaminant selection. Deininger et al. (2000) identify high toxicity, high water solubility, chemical and physical stability, a lack of taste, color and odor, and a low chance of detection with normal analytical methods as being key properties of credible threat contaminants. For chemical contaminants, Khan et al. (2000) use the following criteria to prioritize contaminant credibility: already known to be weaponized, available to potential terrorists, likely to cause major morbidity or mortality, potential of causing public panic and social disruption, and requiring special action for public health preparedness. They list the following as priority chemical agents: arsenic, pesticides, and cyanides. The National Research Council (2002) addresses morbidity and mortality, or toxicity, by focusing on cholinesterase inhibitors, including insecticides (e.g. aldicarb), which act like nerve agents, and are persistent in water. These particular contaminants could be injected in high enough concentration to be harmful to consumers, with the only barrier being the disinfectant residual. The US Army Center for Health Promotion and Preventive Medicine also has listed sodium cyanide and fluoroacetate as priority potential chemical threat agents (Burrows et al., 1997).

Water solubility will frequently be a limiting constraint in determining a credible threat contaminant. Though many potentially highly toxic and available contaminants are soluble in

organic solvents, the solvents themselves contribute a taste, odor, and/or color, or instrument response signature that will in and of itself discredit the contaminant when combined with the solvent from being considered as a credible threat. This was demonstrated when parathion was initially considered in this work.

Contaminants that were used in this research include sodium cyanide, sodium fluoroacetate, aldicarb, and sodium arsenate. Using the criteria specified above, all are considered very credible water threat contaminants.

Beaker tests. The chemical contaminants are all commercially available in powder form. They were measured using an analytical scale[9], and mixed with tap water to obtain the desired stock concentration. The beaker tests were conducted using bench top analytical equipment[10-13]. The distribution system experiments used on-line instruments.

After the 16,000 data point baseline was established using on-line equipment, tap water was added to a beaker, and the parameters were measured using bench top analytical equipment. The four contaminants were then added to the beakers in specified concentrations, and the water quality parameters were measured again, using the same analytical equipment. Finally, the difference was taken between the tap water only measurements and the tap water plus contaminant measurement, and a change in the water quality parameters were determined.

Bench scale distribution system tests. The bench scale distribution system provides the flexibility to conduct controlled experiments to determine on-line contaminant-instrument response in a drinking water distribution system. This is accomplished without compromising simulation of real-world distribution system parameters, including water quality, dilution, flow, and pipe materials.

The bench scale distribution system (Figure 1) had to be built around a ventilation hood to accommodate the safe introduction of very toxic volatile hazardous materials into the distribution system. In addition, the system was designed to discharge hazardous waste under the ventilation hood to ensure safe handling.

Another consideration was hazardous waste minimization. Once the contaminants were introduced into the system, the resulting effluent from the multi-instrument panel was captured and treated as hazardous waste. To reduce the amount of hazardous waste generated, system volume was minimized while still ensuring enough flow to satisfy on-line instrument requirements. To accomplish this goal, one-inch PVC was used to build the pipe loop, providing a system volume of 4.2-liters.

The first data collection effort using the bench scale distribution system established the baseline. In this mode, the contaminant feed system was not used. The only influent to the system was tap water from the local distribution system. The only effluent was from the bench scale distribution system to the two panels, and then the non-hazardous waste effluent from the panels themselves.

The second data collection effort using the bench scale distribution system measured direct contaminant-instrument response. Before contaminants were added, a 100-minute baseline was established to ensure that contaminant-instrument response was compared to water quality just prior to introduction of the contaminants. After the short baseline was established, the system was ready for introduction of contaminants. The influents to the system included the tap water from the local distribution system, and the contaminants that were pumped in using a peristaltic pump[14]. The effluents were from the bench scale distribution system to the two panels, and then the hazardous waste effluent from the multi-instrument panel. The hazardous

waste was redirected with the use of valves and collected under the ventilation hood for proper disposal.

The on-line equipment was started up the night before any distribution system experiments were conducted. In addition, once the peristaltic pump[15] that re-circulates the system water was turned on, it took 1-2 hours for the on-line equipment to stabilize. This is due to the increased flow and turbulence in the system, stirring up particulate matter that may have settled onto the PVC piping. After the monitoring equipment had returned to steady state, and had shown consistent readings, the 100-minute baseline data collection began.

RESULTS & DISCUSSION

Surrogate selection. DeYoung and Gravley (2002) specify that the distribution system provides multiple access points, and is susceptible to injection of contaminants by pumping them in at a higher pressure than the distribution system. The authors further state that some water utility officials believe that <u>the leading threat</u> to the nation's water supply is introduction of a contaminant directly into the distribution system by overcoming system pressure. They emphasize that continuous monitoring capabilities must be developed, that detection is one of three key areas that water supply systems must take action in, and that significant research is needed to detect biological and chemical contaminants.

The focus of this research is on detecting contamination events in the distribution system real-time using water quality parameters that will change significantly in the event of contamination. The parameters that will be used in this study to detect changes in drinking water quality include chlorine residual, turbidity, pH, conductivity, and TOC.

Of the drinking water quality parameters that will be used in this study, chlorine is cited in the literature the most as providing both a barrier to contamination in the distribution system,

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and for use in detecting contamination events. The most prevalent disinfectant in the water industry is chlorine, being used by 80% of large and medium sized utilities, with chloramines being a distant second (Macler et al., 2000). Real-time monitoring of the chlorine residual in the distribution system is not a common practice, but is inexpensive (Clark and Deininger, 2000). To provide safe drinking water to the entire population, the chlorine residual should be monitored at strategic places in the distribution system (Deininger et al., 2000).

The National Research Council (2002) insists that in order to ensure the safety of the water supply, an adequate disinfectant residual, potentially greater than that required by the Safe Drinking Water Act, must be maintained in the distribution system, and that the best line of defense against dangerous bacteria and toxins is maintenance of a high chlorine residual in the distribution system. They emphasize monitoring the chlorine residual in real time at representative locations, and stress that the distribution system has the greatest vulnerability to contamination. Like chlorine, the National Research Council provides a variance in turbidity from baseline properties as an example to detect contamination. Khan et al., (2001) identify the need for research in areas that would use chlorine residual or turbidity in distribution systems with on-line, remote monitoring to detect changes in these parameters.

Deininger (2000) points out that Denver Water has 14 continuous monitoring stations equipped to measure pH, temperature, conductivity, chlorine residual, and turbidity in its distribution system. Clark et. al (2002) highlights chlorine residual and pH as having been previously considered in research as surrogate candidates for on-line monitoring of distribution systems. Finally, Landers (2003) emphasizes the interest in monitoring pH, conductivity, chlorine residual, and turbidity while discussing an EPA award to USGS for real-time monitoring research.

Total organic carbon (TOC) is the only parameter in this study that hasn't been noted in the literature, probably due to cost. Regardless, it is an obvious surrogate for the detection of organic contaminants. As the percentage of organic carbon in the contaminant molecule increases, so will a TOC instrument's response after introduction of the contaminant.

Chlorine residual, turbidity, pH, and conductivity, are all referenced in the literature as good choices of surrogates for detecting distribution system contamination. Total organic carbon is not cited, but is an obvious choice to detect organic contaminants. The drawback to on-line TOC analysis is its high relative cost. Further work may be directed at how effective the other water quality surrogates (chlorine residual, turbidity, pH, conductivity) are at detecting organics without the use of TOC to eliminate this costly equipment from the suite of instruments required to provide robust early warning in the distribution system.

Baseline. The water quality in the distribution system is quantified in terms of the baseline conditions, utilizing on-line analytical equipment to capture multiple parameters every minute. Over 20,000 data points were collected between June-October 2003. Over 16,000 of the data points were collected during a two-week period in June 2003, with the remaining 4,000 being collected 100-minutes immediately before the introduction of contaminants into the distribution system during July-October 2003.

The baseline provided information to determine what is "normal" in the distribution system relative to the time that the data was collected. The standard deviation in the on-line baseline data was used in conjunction with the beaker test data to determine a limit of detection. This will provide the first indication on the potential of using water quality parameters as surrogates to detect a contamination event. The data provided in Table 1 defines baseline drinking water quality conditions relative to the *timeframe* that the data was collected. Figures 2

displays time series plots of the large baseline data set. The time series plots indicate that every parameter behaves differently with respect to time, and that the values of the parameters are in a constant state of flux.

Another consideration is the distribution of the data. Histograms were plotted for the data, and all were quite different for each parameter, and in most cases it was easy to see that the data was not normally distributed. In the case of a suspected normal distribution, for example pH, a look at kurtosis, skewness, and the Anderson-Darling normality test was used in a statistical software package[16] to quantitatively determine if the distribution was normal. Kurtosis measures the peakedness of a distribution, and like skewness, ranges from negative to positive infinity. A kurtosis of zero is one requirement for a Gaussian relationship. Positive kurtosis values indicate narrower and more sharply peaked distributions. Negative values indicate flatter distributions. The kurtosis for the pH data was -0.34. Skewness measures the asymmetry of the data. A Gaussian curve would have a skewness of zero. A positive skewness indicates more values to the left of the mean, a negative skewness indicates more values to the right of the mean. The skewness for the pH data was -0.57. The Anderson-Darling normality test uses a p-value to test the null hypothesis that the data fits a normal distribution. The criteria for normality is a p-value greater than 0.05. The p-value for the pH data was 0.00 indicating that the data does not fit a normal distribution (Gilbert, 1987).

Since the baseline data does not fit well to a normal distribution, a fair question would be "what is the significance of three standard deviations from the mean?" Is the assumption that 99.96% of the baseline data under normal conditions will fall within x-bar (the average or mean) plus or minus three standard deviations (or 3-sigma) valid? To better understand that, the baseline data was analyzed to specifically answer this question. Table 2 provides the percentage

of baseline data points per parameter that fall inside of x-bar plus or minus three-sigma. As Table 2 demonstrates, even for data that is not normally distributed, it is fair to state that any data point outside of x-bar plus or minus three-sigma represents an anomaly.

Figure 2 emphasizes the importance of knowing the baseline water quality real-time in the distribution system, as the water quality is always changing. This is significant, as on-line analysis to detect a contamination event must have an established baseline to compare the suspect data to, at the time that the comparison is taking place. In the absence of timely baseline data, the potential exists to inaccurately determine that an anomalous event has or hasn't taken place. In addition, the ideal of assuming that water quality data in the distribution system can be characterized as fitting a classical normal or log-normal distribution may prove to be erroneous, nullifying any data analysis carried out using such assumptions. However, descriptive statistics and the determination of anomalous events could prove very useful.

Contaminants. Cyanide has been used for thousands of years as a deadly poison to contaminate water. In ancient Rome, Nero eliminated his enemies with cherry laurel water, with cyanide being the toxic ingredient (Sidell et al., 1997). Examples of common cyanide compounds are hydrogen cyanide, sodium cyanide, and potassium cyanide. Sodium cyanide and potassium cyanide are both white solids with a bitter, mild almond-like odor in damp air. Cyanide compounds are used in electroplating, metallurgy, production of chemicals, photographic development, making plastics, fumigating ships, and some mining processes.

Copper ions are key to enzyme operation in every aerobic cell. Cyanide binds to the copper ions in these cells deactivating these essential enzymes. The result is chemical asphyxiation by stopping cell aerobic metabolism. Death can result from a 60-90 mg oral dose (Manahan, 1992).

Sodium fluoroacetate, also commonly known as compound 1080 and sodium monofluoroacetate, is a rodenticide that has been previously used in the United States to control gophers, squirrels, coyotes, and prairie dogs, and is presently banned (Eisler, 1995). Interestingly enough, Verschueren (2001) lists fluoroacetic acid (CAS# 144-49-0) as a chemical warfare agent. Fluoroacetic acid differs from the fluoroacetate ion that makes up sodium fluoroacetate only in the addition of a hydrogen atom, $C_2H_3FO_2$, or in a protonated form. Sodium fluoroacetate is a deadly human poison by ingestion (Sax and Lewis, 1989).

Aldicarb is an extremely toxic, restricted use insecticide. It is a cholinesterase inhibitor, acting in a similar fashion to the nerve agent VX, causing respiratory failure or cardiac arrest due to central nervous system paralysis, potentially leading to death (Manahan, 1992). Baron (1994) discussed two human studies that showed exposure to 0.1 mg/kg or greater of aldicarb resulted in acute cholinergic signs and symptoms.

Prager (1996) describes sodium arsenate, also known as arsenic acid disodium salt, disodium arsenate, and sodium arsenate dibasic, as a clear, odorless powder that is very soluble in water. Sodium arsenate has been previously used in anti-malarial medicine and as an insecticide. Its present uses include poison on fly-papers, toxic ingredient in ant syrups, and as a wood preservative. Norman (1998) states that arsenic can be found in two oxidation states, III and V. This is significant in that the toxicity of arsenic is directly related to its oxidation state. Generally, the arsenic(V) is more chronically toxic, with its toxicity likely a result of its reduction to arsenic(III). Arsenic(III) is acutely toxic, and affects key enzymes including acetylcholine esterase (similar to aldicarb). Chlorine will oxidize arsenic from its most toxic state As^{+3}, to As^{+5}.

Table 3 provides information on the toxicity of the water contaminants that were used in this research effort. The minimum concentration in a glass of water to reach the LD_{50} is based on a 60 kg person drinking a 0.5 L glass of water. In addition, physical and chemical properties of these same contaminants are provided.

Beaker tests. Beaker tests were conducted before the contaminants were introduced into the bench scale distribution system. There were three primary objectives behind conducting the beaker tests: to determine which parameters would be directly influenced by specific contaminants, to determine the approximate minimal concentration that contaminants in a controlled environment would impact water quality, and to anticipate concentrations that would be pumped into the bench scale distribution system.

In addition, the beaker tests served as indicators of the actual concentration that the on-line instruments saw. The contaminants were pumped into the bench scale distribution system at known concentrations, and then diluted due to mixing within the system before flowing through the instrument panels. At this point, the contaminant concentration flowing through the panels was an unknown. The beaker tests provide an indication of the concentration flowing through the on-line panels, similar to a calibration curve.

Figures 3-5 provide changes from baseline water quality parameters after a contaminant was added to tap water at the specified concentration. In addition, toxic contaminant concentrations are provided to allow comparison of the limit of detection and the concentration that would cause potential serious illness. All of the toxic concentrations are much lower than the human oral LD_{50} values as indicated in Table 3.

The 3σ line represents an estimate for the limit of detection for a contamination event using the water quality surrogate specified. Theoretically, 99.96% of the data points under

"normal" conditions will fall within three standard deviations and anything outside of the three sigma line will represent a non-random deviation in the signal. More importantly, as seen in Figures 3 and 4, the limit of detection is much lower than the corresponding dangerous contaminant concentrations.

As noted in Figure 3, the limit of detection of sodium fluoroacetate using a change in chlorine residual is approximately 16 mg/L. This is good news, in that the "highly dangerous concentration" of sodium fluoroacetate is 60 mg/L. Ideally, the goal is always to detect these contaminants at the lowest possible concentration. To be able to directly detect a contaminant at a concentration below that which would result in considerable health impacts is the goal of monitoring.

The TOC curve levels out at the instrument's maximum published TOC range of 10 mg/L. Again, the limit of detection is much lower than the specified concentration that would cause significant health impact. A comparison between the two charts in Figure 3 may provide justification for the cost of a TOC analyzer. As can be seen, the TOC analyzer's limit of detection for sodium fluoroacetate was 1.5 mg/L, significantly lower than using chlorine residual (16 mg/L). This result should be expected for organic contaminants, with molecules having more organic carbon being detected at lower concentrations than those having less. Figure 4 provides a similar result. Sodium cyanide was detected well below the "life threatening toxicity" using pH as a surrogate. Of the four contaminants, cyanide was the easiest to detect, changing all of the water quality parameters significantly at relatively low concentrations.

Even though cyanide is an inorganic compound, sodium cyanide elicited a significant instrument response from the TOC analyzer at a concentration well below the point of significant health impact. It is thought that the low-temperature UV-persulfate oxidation analysis method

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used in the TOC analyzer was not effective at purging the triple-bonded carbon-nitrogen molecule, so the carbon remained and was oxidized to carbon dioxide, and therefore detection as TOC was complete.

Figure 5 displays changes in conductivity after varying concentrations of sodium arsenate was added to tap water in a beaker. This figure demonstrates a requirement to reduce the limit of detection for certain contaminants, as direct detection using water quality surrogates will not suffice to protect public health. As can be seen, sodium arsenate is detected *above* the concentration of concern. The published value for sodium arsenate toxicity was the U.S. Army's "life threatening toxicity" for inorganic arsenic of 14 mg/L (USACHPPM TG 230, 2002).

Figures 3 and 4 demonstrate the potential of using on-line water quality monitoring to detect contamination events at concentrations below those that would cause significant health effects. Figure 5 demonstrates the need for more sophisticated data analysis techniques to reduce the limit of detection. Consideration may be given to data mining techniques that would take the large quantity of on-line generated data, and use pattern recognition techniques or artificial neural networks to further reduce the limit of detection obtained by direct on-line analysis.

Bench scale distribution system tests. Before introducing the contaminants into the bench scale distribution system, data was collected for 100 minutes to determine baseline conditions. The values in Table 4 indicate the lowest concentration that the contaminant was detected at using the water quality parameter in the column heading. These values are the result of comparing the change in the water quality parameter to both the three-sigma value from the 100-minute baseline, and the published instrument error. Highlighted values indicate the lowest limit of detection, or a recommended water quality surrogate for detecting that contaminant.

Table 4 provides encouraging results. All four contaminants were detected at relatively low concentrations using the on-line equipment whereas only three of the four were detected at low enough concentrations using the beaker tests and bench top analytical equipment. The key difference is using the on-line turbidimeters to detect sodium arsenate. The "life threatening toxicity" for inorganic arsenic of 14 mg/L was discussed previously for evaluation of the beaker test data. The on-line data suggests that sodium arsenate may be detected at concentrations below 15 mg/L, or a lot closer to the concentration of concern than conductivity was able to detect (~27 mg/L as shown in Figure 5).

Figure's 6 through 9 are time series plots showing the on-line instrument response after the contaminants are pumped into the bench scale distribution system at varying concentrations. The first 100-minutes are baseline conditions. With the contaminant pump turned on at t=100 minutes, it took four minutes to feed the one-liter of contaminant into the system.

Conductivity showed the most significant instrument response for sodium arsenate. Sodium cyanide and sodium fluoroacetate also had measurable instrument responses for conductivity. Sodium cyanide significantly changed all of the water quality parameters at relatively low concentrations. It was the only contaminant that significantly changed pH. Aldicarb affected the chlorine residual quickly, as did sodium cyanide. Aldicarb and sodium fluoroacetate increased the TOC as would be expected, with the aldicarb molecule containing more carbon, and eliciting a more significant instrument response.

CONCLUSIONS

The threat of chemical or microbiological contamination to drinking water is well established and requires an urgent effort to protect our drinking water systems from malevolent acts of sabotage. As it presently stands, the technology to detect these contaminants is lacking.

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Early detection of these contaminants via on-line or real-time monitoring has been identified as a feasible way to provide early warning to protect public health.

Results from this study indicate that routine water quality instruments can detect chemical disturbances in drinking water distribution systems at relatively low concentrations. Three of the four contaminants were detected well below concentrations of concern. The fourth, sodium arsenate, was detected near the "life threatening toxicity" concentration using on-line monitoring of turbidity.

In an effort to reduce the limit of detection further, potential may lie in applying statistical pattern recognition or artificial neural networks to the large data sets available from on-line monitors. In addition, is there a potential to derive some good from biofilms that are typically in the distribution systems? By using the sloughed-off biomass that may occur after the introduction of a toxic contaminant to a drinking water distribution system, perhaps turbidity would increase, signaling a contamination event. Finally, on-line TOC analysis has proven very helpful in reducing the limit of detection for organic contaminants. If the cost of on-line TOC analyzers proves prohibitive for some utilities, an effort to quantify changes in other water quality parameters when organic contaminants are added to drinking water may offer a viable option.

The results of this research indicate that routine monitoring can be used in the distribution system to detect a range of contaminants real-time, potentially providing adequate early warning to take appropriate action and protect public health. In addition to detecting intentional threat contaminants in a distribution system, real-time monitoring offers the secondary benefit of providing valuable water quality data that may be key to detecting routine water quality

compromises associated with line breaks, backflow events, treatment plant failures, or seasonal biofilm sloughing.

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FOOTNOTES

[1]Distribution monitoring panel, Hach Co., Loveland, Colo.
[2]Astro autoTOC 1950plus process TOC analyzer, Hach Co., Loveland, Colo.
[3]OPC datalogger, Hach Co., Loveland, Colo.
[4]GLI P53 pH/ORP analyzer, Hach Co., Loveland, Colo.
[5]CL17 chlorine analyzer, Hach Co., Loveland, Colo.
[6]1720D/L low range process turbidimeter, Hach Co., Loveland, Colo.
[7]FT660 laser light nephelometer, Hach Co., Loveland, Colo.
[8]GLI C53 conductivity analyzer, Hach Co., Loveland, Colo.
[9]AE100 Analytical Balance, Mettler-Toledo, Inc., Toledo, OH
[10]AR25 pH meter, Fischer Scientific, Pittsburgh, PA
[11]Hach 2100 AN turbidimeter, Hach Co., Loveland, Colo.
[12]DR/3000 spectrophotometer (for chlorine residual), Hach Co., Loveland, Colo.
[13]ECTestr Low conductivity meter, Oakton Instruments, Vernon Hills, IL
[14]MasterFlex 7016-20/7521-40 peristaltic pump, Cole-Parmer Instrument Co., Vernon Hills, IL
[15]MasterFlex 77601-10/7591-50 peristaltic pump, Cole-Parmer Instrument Co., Vernon Hills, IL
[16]MINITAB Statistical Software v13, Minitab Inc., State College, PA
[17]Confidential Source
[18]Norman (1998)
[19]Krieger (2001)
[20]USACHPPM (2002)

DISCLAIMER: The opinions and conclusions in this paper are the author's alone and do not necessarily reflect those of the United States Air Force, or the Federal Government.

TABLES

Table 1 On-line monitoring baseline water quality results.

	Chl Res (mg/L)	Conduct (uS/cm)	pH	TOC (mg/L)	Turbidity (NTU)	Laser Turbidity (NTU)
Min	0.33	113.91	7.66	1.17	0.08	0.06
Avg	0.52	120.96	7.88	1.92	0.11	0.10
Max	0.86	131.50	8.06	2.24	0.75	1.00
3σ	**0.20**	**14.08**	**0.25**	**0.56**	**0.07**	**0.12**

Table 2 Percentage of baseline data points falling within x-bar +/- 3σ.

Conductivity (uS/cm)	PH	Turbidity (1720D) (NTU)	Turbidity (Laser) (NTU)	Chlorine Residual (mg/L)	TOC (mg/L)
100.00%	100.00%	98.34%	98.65%	99.02%	96.58%

Table 3 Properties of interest for credible threat chemical contaminants.

Property	Sodium Fluoroacetate	Aldicarb	Sodium Cyanide	Sodium Arsenate
Human Oral LD$_{50}$ (mg/kg)	2-5[17]	0.8[18]	3-7[17]	20[19]
Min Concentration in glass of water to reach min human oral LD$_{50}$	240 mg/L	96 mg/L	360 mg/L	2,400 mg/L
Life-Threatening Toxicity	60 mg/L[20]	Not available	48 mg/L[21]	14 mg/L[21]
EPA SDWA MCL	N/A	N/A	0.2 mg/L	10 ug/L
CAS #	62-74-8	116-06-3	143-33-9	7778-43-0
Chemical Formula	$C_2H_2FO_2Na$	$C_7H_{14}N_2O_2S$	NaCN	Na_2HAsO_4
Molecular Weight	100.03	190.25	49.01	185.9
Soluble in Water	extremely	0.6 g/100mL	highly soluble, 37 g/100 mL	61 g/100 mL
Stability in Water	$t_{1/2}$=2-6 days in water	Very Stable	Very Stable	Stable

Table 4 Limits of detection for contaminants for each water quality surrogate.

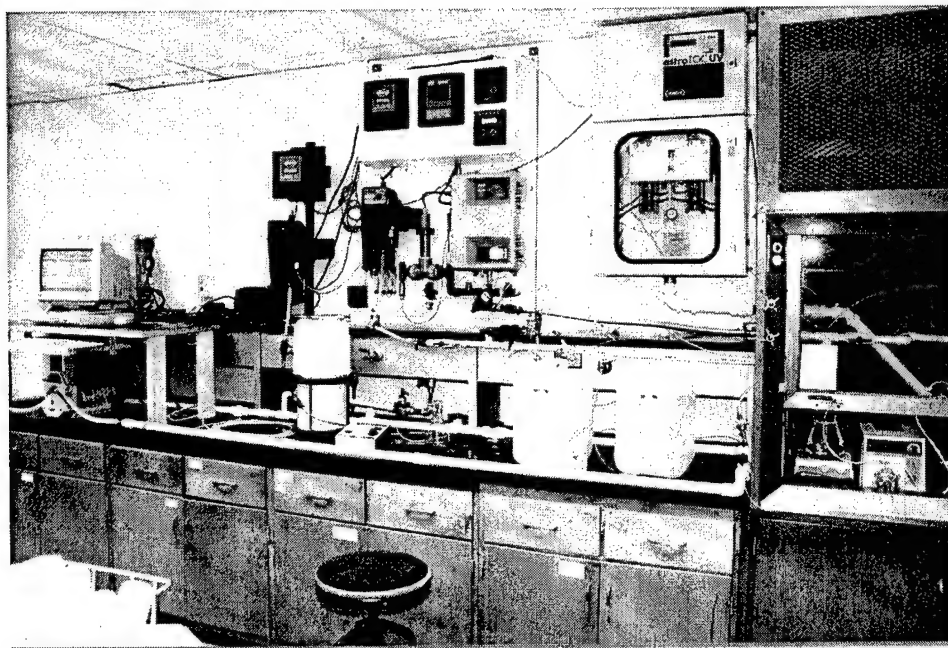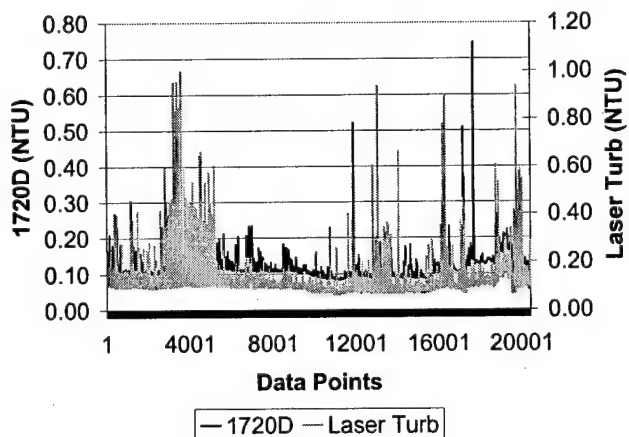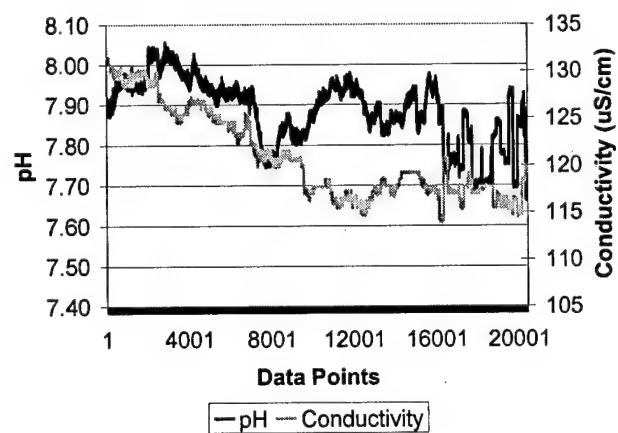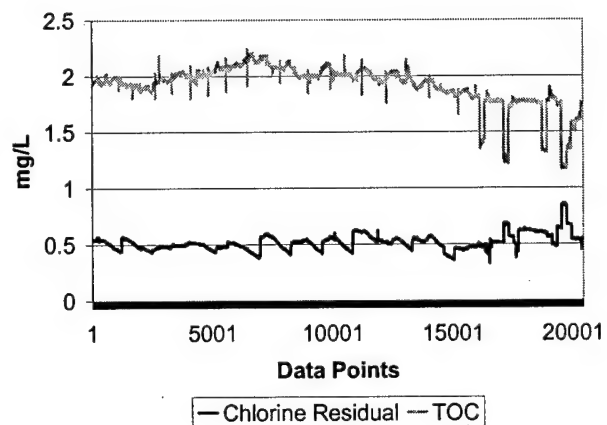| Contaminant	Chlorine Residual	Conductivity	pH	TOC	Turbidity	Laser Turb
Sodium Arsenate (mg/L)	>100	25	>100	>100	<15	<15
Sodium Cyanide (mg/L)	<0.5	5	1	>10	<0.5	1
Sodium Fluoroacetate (mg/L)	10	10	3	10	3	3
Aldicarb (mg/L)	1	>10	1	3	3	3

FIGURES

Figure 1 Bench scale distribution system.

Figure 2 Baseline water quality time series plots.
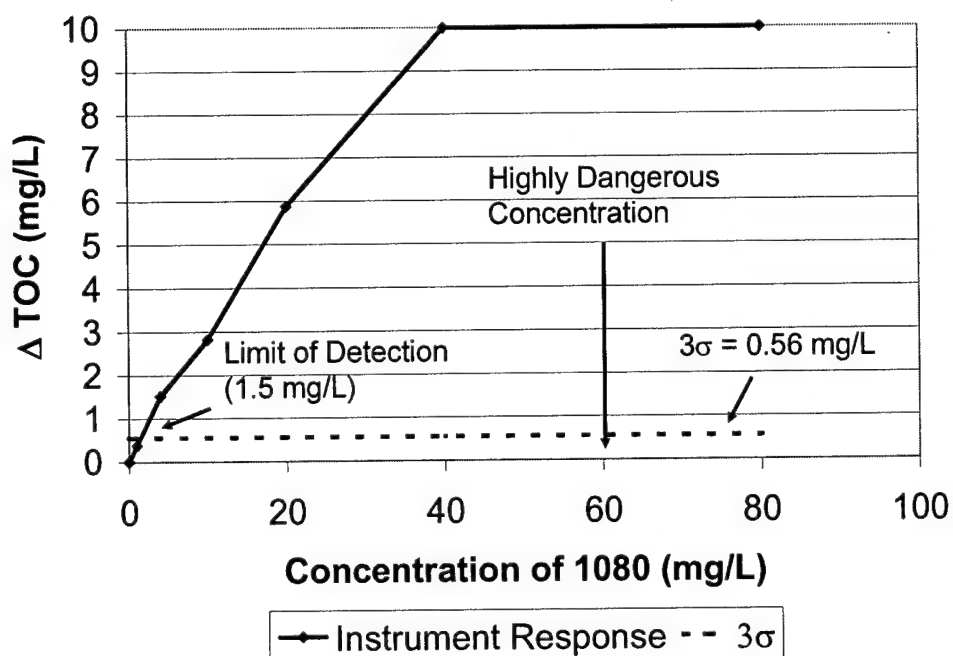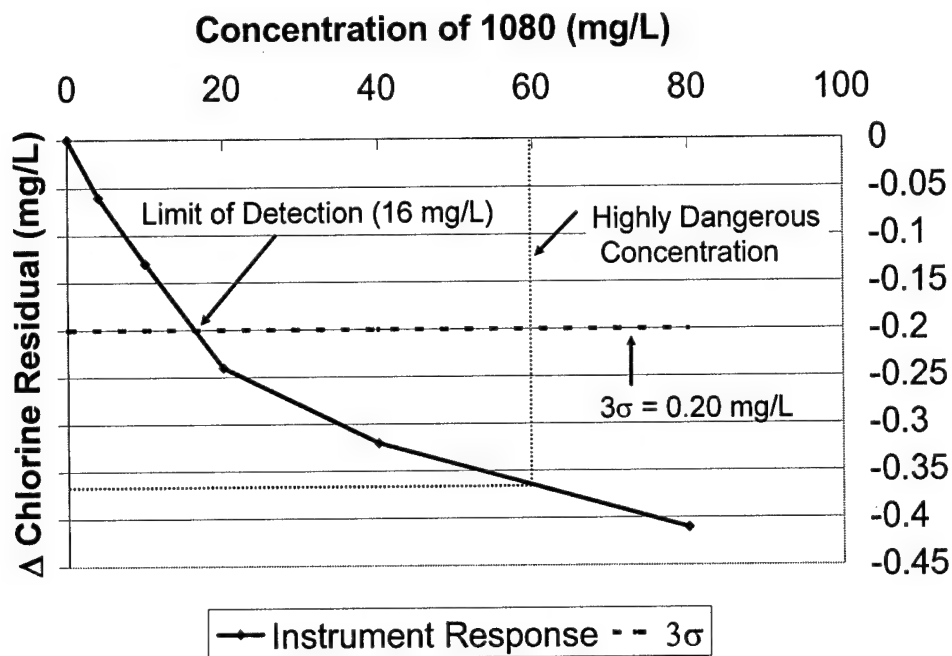
Figure 3 Concentration-instrument response for sodium fluoroacetate (1080), chlorine residual, and TOC.
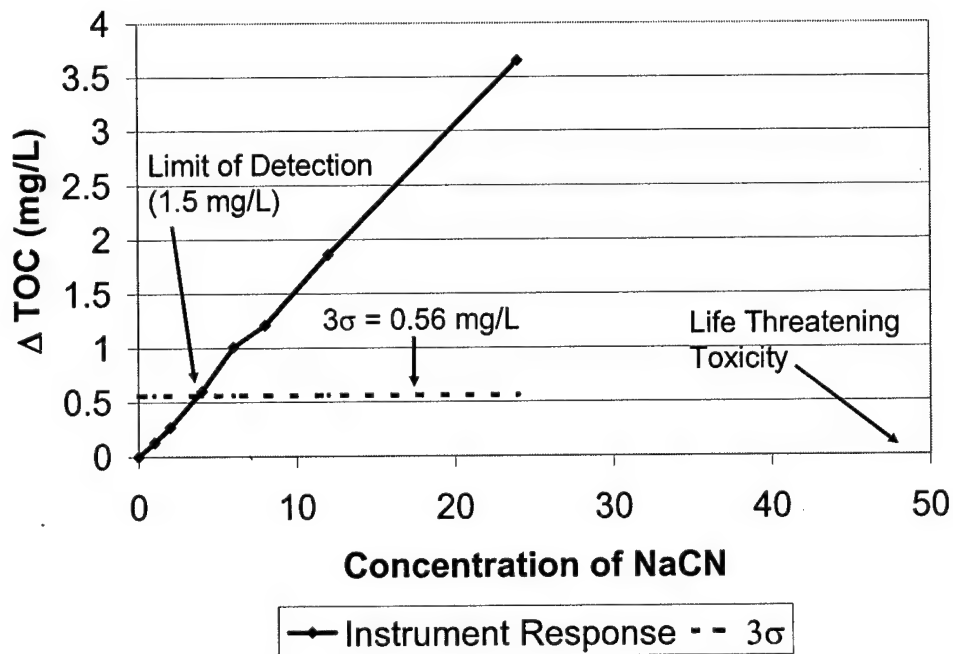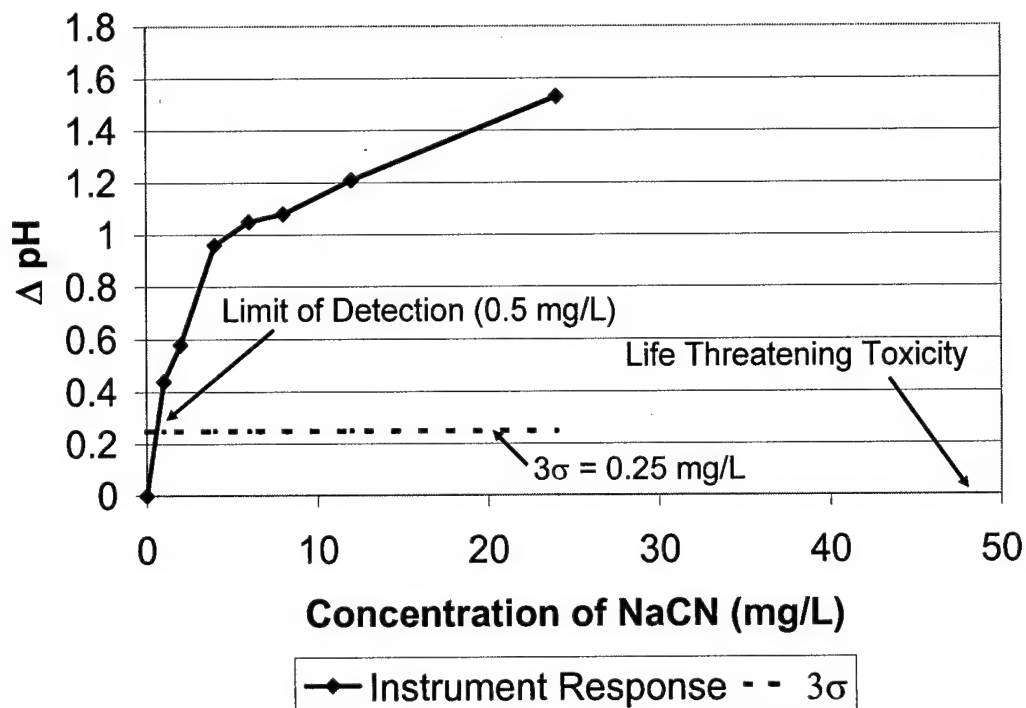
Figure 4 Concentration-instrument response for sodium cyanide, pH, and TOC.
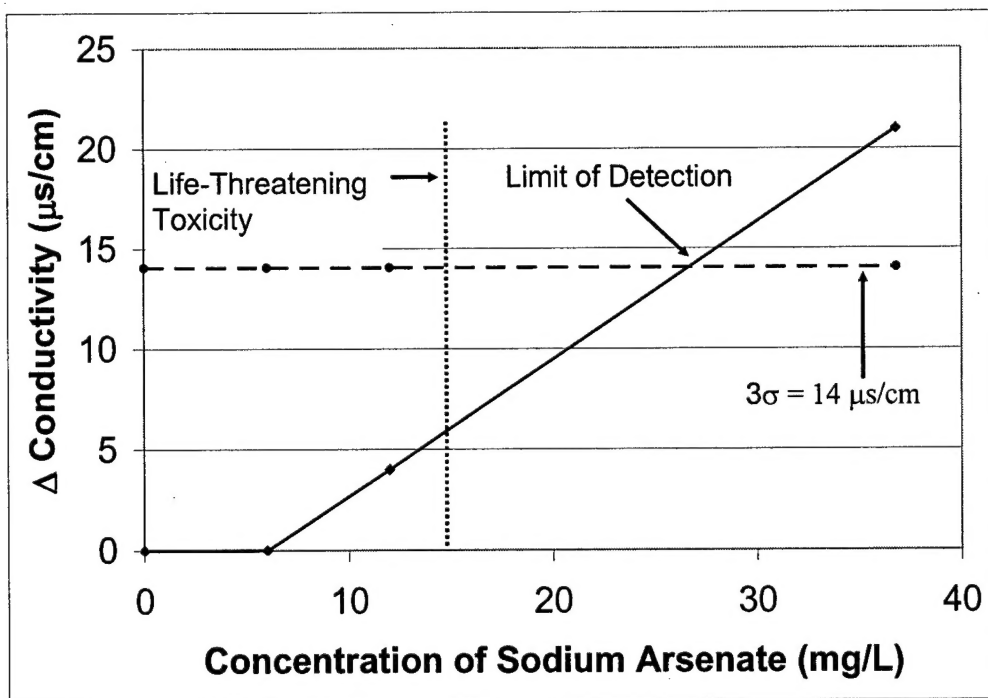
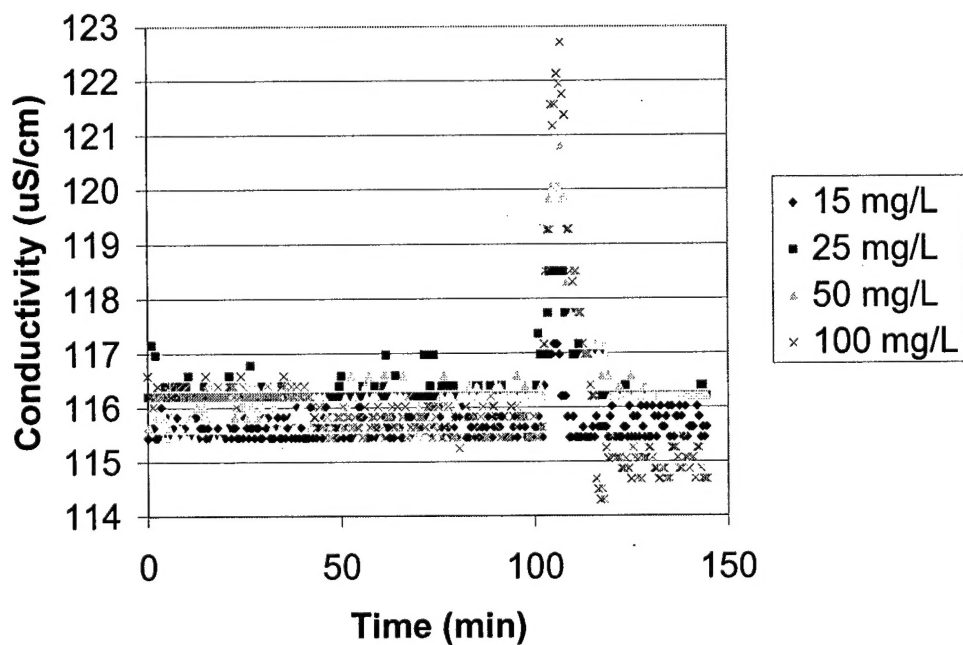**Figure 5** Concentration-instrument response for sodium arsenate and conductivity.

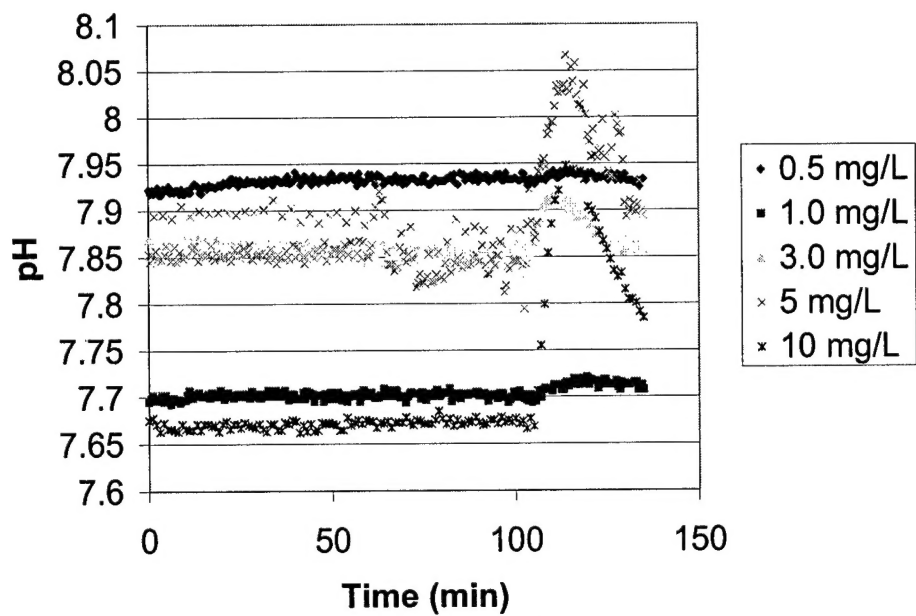**Figure 6** Time series plot of on-line instrument response for sodium arsenate and conductivity.

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Figure 7 Time series plot of on-line instrument response for sodium cyanide and pH.
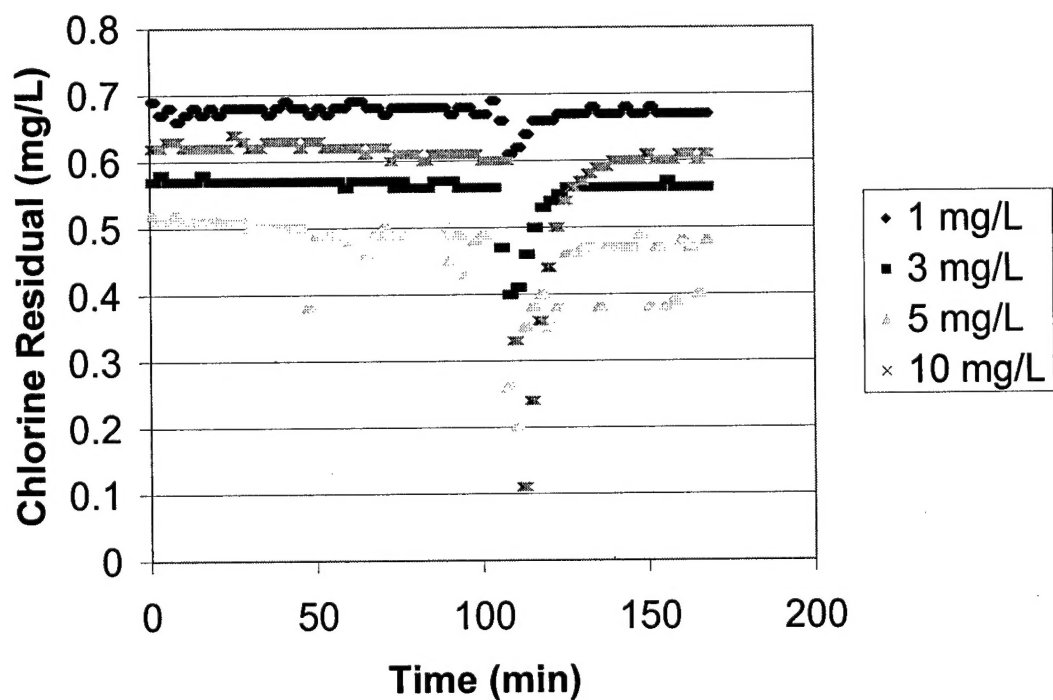

Figure 8 Time series plot of on-line instrument response for aldicarb and chlorine
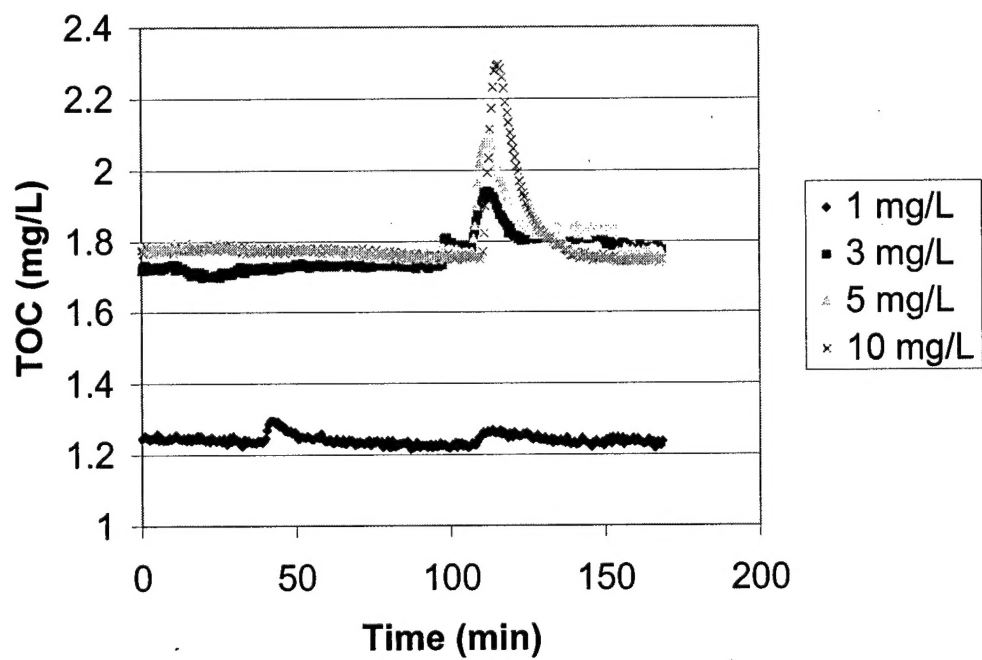
residual.

Figure 9 Time series plot of on-line instrument response for aldicarb and TOC.

REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	23.Feb.05	MAJOR REPORT

4. TITLE AND SUBTITLE
REAL-TIME DETECTION OF INTENTIONAL CHEMICAL CONTAMINATION
IN THE DISTRIBUTION SYSTEM

5. FUNDING NUMBERS

6. AUTHOR(S)
MAJ BYER DAVID E

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
COLORADO STATE UNIVERSITY

8. PERFORMING ORGANIZATION REPORT NUMBER

CI04-965

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
THE DEPARTMENT OF THE AIR FORCE
AFIT/CIA, BLDG 125
2950 P STREET
WPAFB OH 45433

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Unlimited distribution
In Accordance With AFI 35-205/AFIT Sup 1

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

14. SUBJECT TERMS

15. NUMBER OF PAGES
33

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT